



## Negative plate discharge in lead acid batteries. Part I: General analysis, utilization and energetic coefficients

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### Abstract

The process of negative plate discharge in lead acid batteries from two manufacturers has been investigated at low current densities. The discharge curves and specific capacities, at several H<sub>2</sub>SO<sub>4</sub> concentrations (2.3–7.0 M) and current densities (0.5–3.2 mA cm<sup>-2</sup>), showed that the negative plate discharge includes solid state reactions. When these results were put beside those previously obtained for positive plates, they showed that the processes of positive and negative plate discharges are different and an explanatory theory has been proposed. By analysing the utilization coefficient together with the specific capacities, the different roles of the nucleation processes at the positive and negative plates were revealed. Finally, the determination of the energetic coefficient proved to be useful in evaluating the quality of manufacture of the active material.

### 1. Introduction

The lead acid battery and its active material have been the subject of a large number of publications [1], specially for the case of positive plates. The negative plate and its active material has not received as much attention and publications have been sparser [1–5]. In the negative plates, several additives can solve problems such as self-discharge, nucleation, electronic connectivity and volume variations in the active material and ensure a longer cycle life than for the positive plate. Possibly, this better performance has led researchers to concentrate attention in the positive plate.

The present paper aims to enhance understanding of negative plate behaviour. Determinations of charge and discharge curves, specific capacities, utilization and energetic coefficients, under different conditions, were made. In the last case a recently published method [6] was applied. The work also shows that studies of negative plates may contribute to a better understanding of the positive plate.

### 2. Experimental details

Galvanostatic discharges were carried out on full size negative plates from SLI 36 Ah batteries produced by two different manufacturers. These plates were identified as plate-A (67 g of active material, 1.0 mm grid rod

diameter with 3.2 wt % Sb) and plate-H (64 g of active material, 0.8 mm grid rod diameter with 1.8 wt % Sb), both having the same 50% v/v macroporosity in the active material and a geometrical area of 280 cm<sup>2</sup> (140 cm<sup>2</sup> on each side) relative to which the charge ( $i_{ch}$ ) or discharge ( $i_d$ ) current density values are given. The latter are also given, in some cases, as mA per gram of active material.

Before being disassembled, the batteries were submitted to five stabilization cycles. Each stabilization cycle consisted of a 4.3 mA cm<sup>-2</sup> (18.0 mA g<sup>-1</sup>) discharge followed by a 2.1 mA cm<sup>-2</sup> (8.8 mA g<sup>-1</sup>) charge, continued until the battery was fully charged.

After stabilization, the batteries were disassembled and each negative plate was fitted rigidly between two positive plates, 7 mm from each one to constitute the electrochemical cell. Such an arrangement ensures a constant H<sub>2</sub>SO<sub>4</sub> concentration in the solution outside the plate during the charge–discharge experiments.

Galvanostatic discharges were performed in different H<sub>2</sub>SO<sub>4</sub> concentrations between 2.3 and 7.0 M and different  $i_d$  between 0.5 and 3.2 mA cm<sup>-2</sup>. After each galvanostatic discharge at a given concentration, the negative plates were recharged at an  $i_{ch}$  of 1.6 mA cm<sup>-2</sup> for at least 30 h. Then, they were kept at a floating potential of 2.3–2.4 V per cell for at least 72 h up to the start of next experiment.

To change from one concentration to another, after recharging, the electrochemical cell was filled with the

new solution several times, allowing time for homogenization of the concentrations inside the plates at each step. The measurements were made going from the lowest to the highest concentration.

In all experiments, temperature was maintained at 25 °C and potentials ( $E$ ) were measured against a Hg/Hg<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> 4.6 M reference electrode.

### 3. Results and discussion

#### 3.1. Discharge process

Results from low rate galvanostatic discharges for negative plate-A in 3.5 M H<sub>2</sub>SO<sub>4</sub> solution are shown in Figure 1. These are typical plots of potential against time at different  $i_d$ . The same kinds of plots for different acid concentrations, at two  $i_d$ , are presented in Figures 2 and 3 for the same kind of plates. The analysis of such plots shows some different features from those obtained in previous work with positive plates [6], under equivalent experimental conditions.

When the negative plates are galvanostatically discharged directly through a galvanostatic anodic-cathodic current step, without any resting period, the nucleation peak potential at the beginning of the discharge is smaller than that for positive plates, under equivalent conditions. Since those peaks are a demonstration of a nucleation process occurring, the shortening of the nucleation peak in the negative plates can be attributed to the presence of BaSO<sub>4</sub> in the negative plate. This additive acts as a nucleation agent, making a higher peak potential unnecessary. It is well known [7] that BaSO<sub>4</sub> is isomorphous with PbSO<sub>4</sub> and hence its particles act as nucleation sites for the formation of the PbSO<sub>4</sub> phase.

After the small peak in the discharge curves, there is the regular plateau associated with the advance of the reaction inside the active material. The interesting point

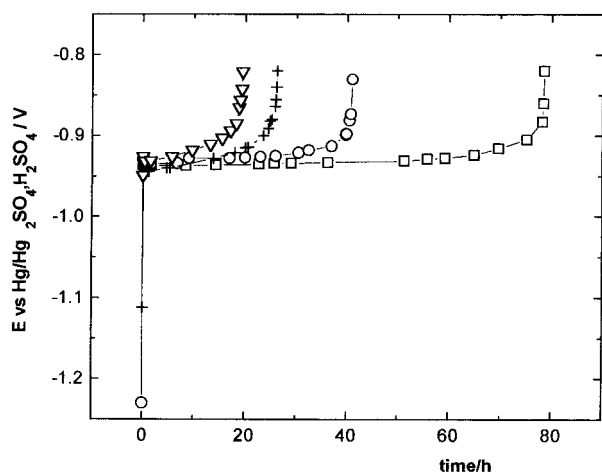


Fig. 1. Typical discharge plots for negative plates-A in 3.5 M H<sub>2</sub>SO<sub>4</sub>. Low discharge current densities: (□) 0.5, (○) 1.1, (+) 1.6 and (▽) 2.1 mA cm<sup>-2</sup>.

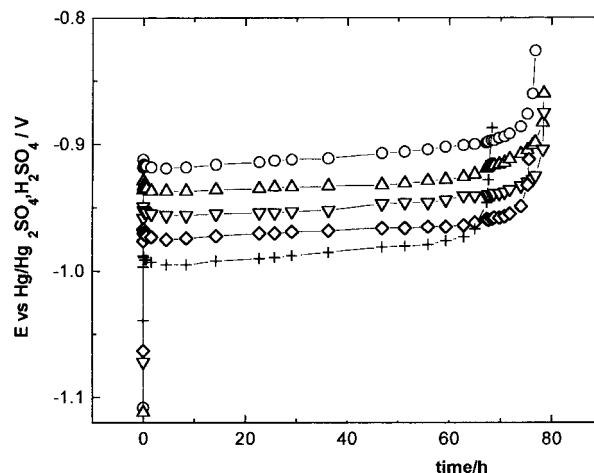


Fig. 2. Typical discharge plots for negative plate A in various H<sub>2</sub>SO<sub>4</sub> concentrations.  $i_d = 0.5 \text{ mA cm}^{-2}$  (2.1 mA g<sup>-1</sup>). Key: (○) 2.3, (△) 3.5, (▽) 4.6, (◇) 5.5 and (+) 7.0 M.

is that the potential in the plateau range, for a given discharge ( $Q_d$ ), decreases linearly as the acid concentration increases. This is shown in Figure 4 for two values of  $i_d$ . Furthermore, each straight line plotted in Figure 4 has the same slope as that for the rest potential (potential of zero current) plots versus sulfuric acid concentration [8]. Therefore, the overpotential ( $\eta$ ) for the discharge of the negative plates, at the same current density and amount of discharge  $Q_d$ , is independent of the sulfuric acid concentration. In other words, for the same stage of discharge, the ohmic voltage drop in the plateau region does not vary with the H<sub>2</sub>SO<sub>4</sub> concentration. This is an indication that the drop is acting through a film and not through the solution at this stage of the discharge.

Another interesting result in support of this hypothesis concerns the average resistance of the negative plate, defined as  $(\partial E / \partial i_d)_{Q_d}$ , within the plateau region. Here  $Q_d$  is once more a chosen amount of discharge in the plateau region. The defined average resistance was

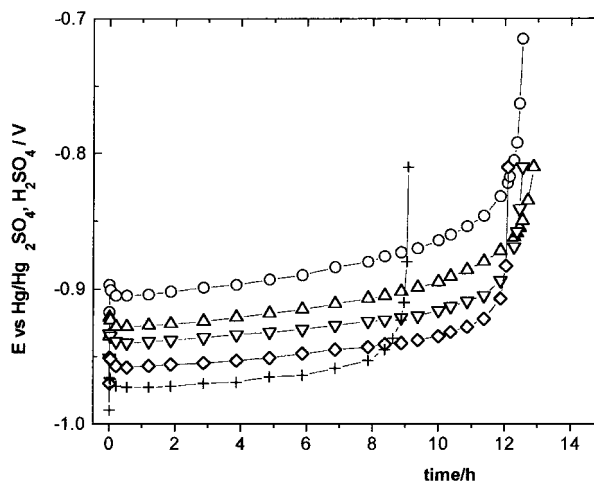


Fig. 3. Typical discharge plots for negative plate A in various H<sub>2</sub>SO<sub>4</sub> concentrations.  $i_d = 3.2 \text{ mA cm}^{-2}$  (12.5 mA g<sup>-1</sup>). Key: (○) 2.3, (△) 3.5, (▽) 4.6, (◇) 5.5 and (+) 7.0 M.

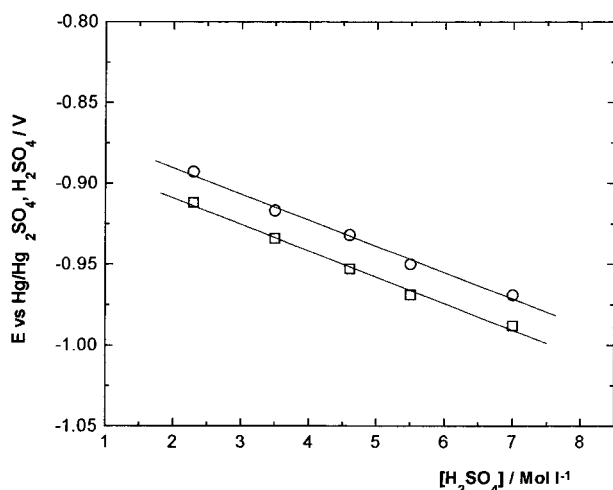


Fig. 4. Plateau potentials against sulfuric acid concentration for two current densities. Data obtained from Figures 2 and 3 at an amount of discharge  $Q_d$  of 15.1 kC per plate. Key: (□) 0.5 and (○) 3.2 mA cm<sup>-2</sup>.

found to be constant, independent of the discharge current densities and acid concentrations. This is demonstrated in Figure 5 where the potential in the plateau region for a given  $Q_d$  is plotted against  $i_d$ , for different  $H_2SO_4$  concentrations.

The plots in Figure 5 all give an average resistance of about 8.5  $\Omega$  cm<sup>2</sup>. This means that, in the plateau region, and for the same  $Q_d$ , the ohmic resistance of the process at the same stage of discharge is once again independent of current density and acid concentration. This is another experimental indication that, within the plateau, the average resistance is produced by something resembling a solid state reaction through a growing film.

Finally, at the end of the plateau, there is a fast increase of potential, indicating the end of the discharge. The interpretation of this is, traditionally, associated with the acid concentration decreasing inside the pores. However, in the present work the effect of this must be

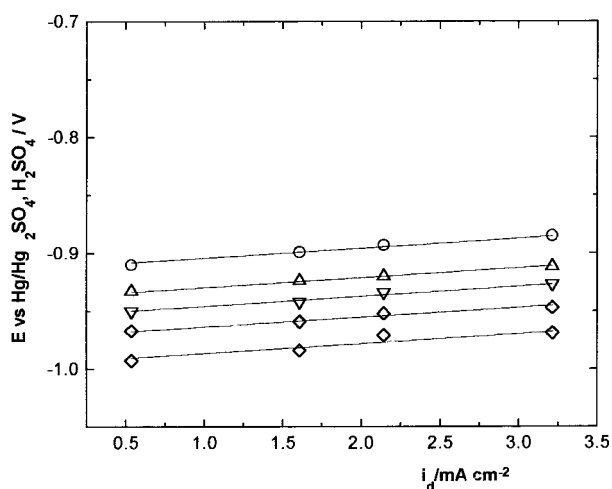


Fig. 5. Potentials in the plateau range against current density for various sulfuric acid concentrations.  $Q_d = 21.6$  kC/plate. Average slope = 8.5  $\Omega$  cm<sup>2</sup> (= 30 m $\Omega$  per plate). Key: (○) 2.3, (△) 3.5, (▽) 4.6, (◇ upper) 5.5 and (◇ lower) 6.9 M.

less important, owing to the low discharge rates and the excess of acid. These conditions provide enough acid replenishment in the active material, through macroporosity. This increase of potential must be due to the fact that the solid state reaction occurring in the plateau cannot continue to maintain the applied current density. This must happen when the advance of the reaction has to cover the whole inner surface of the active material.

### 3.2. Specific capacity

The variation of the specific capacity of negative plates A and H with sulfuric acid concentration, at various low discharge current densities, is plotted in Figures 6 and 7, respectively. Plate A specific capacity is higher than that of plate H and both capacities fall as acid concentration rises, more steeply at the highest concentration.

The higher specific capacity values for plates A indicates an intrinsic difference between the two manufacturing technologies. Since their macroporosities are the same, this difference must certainly be related to the differences in microporosity.

The decrease in specific capacity with increase in acid concentration, up to about 5 M  $H_2SO_4$ , seen in Figures 6 and 7, could be related to a general passivity phenomenon [9]. According to the passivation theory, when the concentration of the anion forming the film is increased, the thickness of the final passivation film is reduced. The data are in agreement with the fact that the  $SO_4^{2-}$  concentration increases with the formal sulfuric acid concentration up to approximately 7.0 M [10]. The fall in specific capacity at the highest concentrations will be discussed later.

Considering all the data presented, the formation of  $PbSO_4$  on Pb must follow equivalent steps to those occurring on the positive plate [11]. During discharge, the negative plate must undergo a passivation process that takes place through nucleation, growth of the nucleus to form a continuous film, thickening of the film

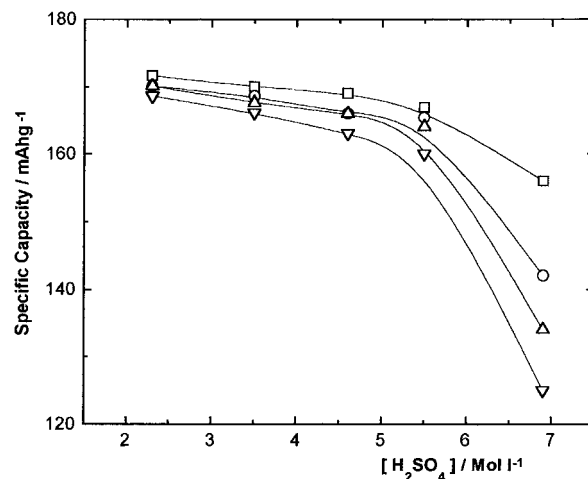


Fig. 6. Typical plots of specific capacity of negative plate A against sulfuric acid concentrations at 25 °C and for different low discharge current densities. Key: (□) 0.5, (○) 1.6, (△) 2.1 and (▽) 3.2 mA cm<sup>-2</sup>.

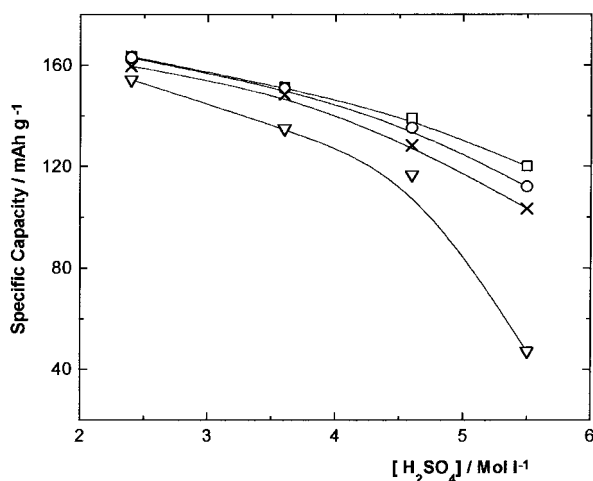


Fig. 7. Typical plots of specific capacity of negative plate H against sulfuric acid concentrations at 25 °C and for low discharge current densities. Key: ( $\square$ ) 0.5, ( $\circ$ ) 1.6, ( $\times$ ) 2.0 and ( $\nabla$ ) 3.0 mA cm<sup>-2</sup>.

and, finally, rupture of the film and recrystallization. These stages will occur successively at each point of the inner surface of the active material, during the advance of the whole reaction, from the surface of the plate to the inner parts.

With this in mind, it is interesting to compare the behavior of negative plates with that of positive plates by applying the empirical equation ( $\log C$  against  $i_d$ ) proposed for the positive plates [6] and valid for very low discharge rates. These results are presented in Figures 8 and 9 for plates A and H, respectively.

A significant point to note in these figures is that the extrapolation of  $\log C$  to  $i_d$  zero does not give the same constant value ( $C_0$ ) for different concentrations, as it did for positive plates [6]. This is in agreement with the hypothesis that the discharge of the positive plates first forms PbO [11]. Thus, in the case of positive plates, PbSO<sub>4</sub> is generated by a reaction of the intermediate PbO with H<sub>2</sub>SO<sub>4</sub>. This means that the maximum

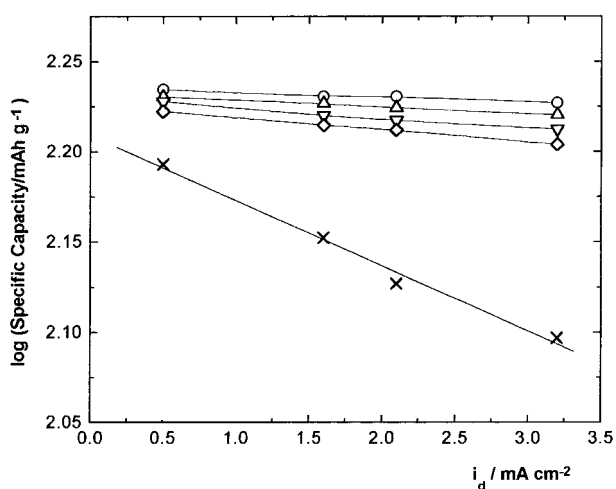


Fig. 8. Log  $C$  against  $i_d$  for negative plate A at very low discharge rates and in different H<sub>2</sub>SO<sub>4</sub> concentrations. Key: ( $\circ$ ) 2.3, ( $\Delta$ ) 3.5, ( $\nabla$ ) 4.6, ( $\diamond$ ) 5.5 and ( $\times$ ) 7.0 M.

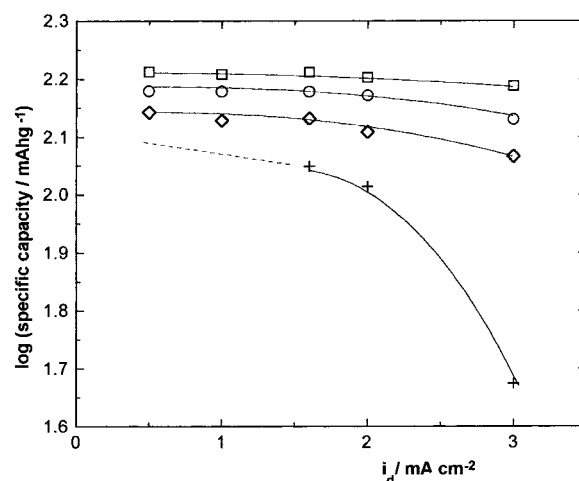


Fig. 9. Log  $C$  against  $i_d$  for the negative plate H at very low discharge rates and in different H<sub>2</sub>SO<sub>4</sub> concentrations. Key: ( $\square$ ) 2.4, ( $\circ$ ) 3.6, ( $\diamond$ ) 4.5 and (+) 5.5 M.

amount of discharge of the positive plate is determined not by the H<sub>2</sub>SO<sub>4</sub> concentration, but by the amount of generated PbO, which depends on the number of its formed nuclei [11]. In other words, the transformation that gives rise to  $C_0$  would be determined by the previously formed amount of PbO. Consequently, in positive plates the process is not related to the acid concentration.

In contrast, for negative plates, the H<sub>2</sub>SO<sub>4</sub> concentration must have an effect on the discharge, since PbSO<sub>4</sub>, in this case, is generated without an intermediate on the surface of the active material.

Another point that must be emphasized is the slow decrease of  $C$  in Figures 8 and 9 as the current density increases, at least for the lower acid concentrations used. This does not happen in the positive plate and can be explained by the fact that, at low discharge rates, the nucleation in the negative plate must happen mainly on the BaSO<sub>4</sub> particles. The weak dependence of  $C$  on current density will correspond to the small variation in the number of nuclei, which depends essentially on the amount and kind of particles of BaSO<sub>4</sub>.

Finally, the higher rate of decrease of  $C$  with rising  $i_d$  seen at the highest acid concentration (7.0 M for plate A and 5.5 M for plate H) must be related to the fact that, in this situation, there is significant nucleation of PbSO<sub>4</sub>, not only on BaSO<sub>4</sub>, but also directly on Pb. Under these conditions the increase in  $i_d$  will increase the number of nuclei of PbSO<sub>4</sub> on the Pb surface and so, there will be a high decrease of the thickness of the produced film. As a consequence, there will be a greater decrease of the specific capacity with  $i_d$ .

### 3.3. Concentration effects on the utilization and energetic coefficients

Typical results for the utilization coefficients ( $\alpha$ ) for negative plates A and H under low rates of discharge (Figure 10) strongly support the ideas previously devel-

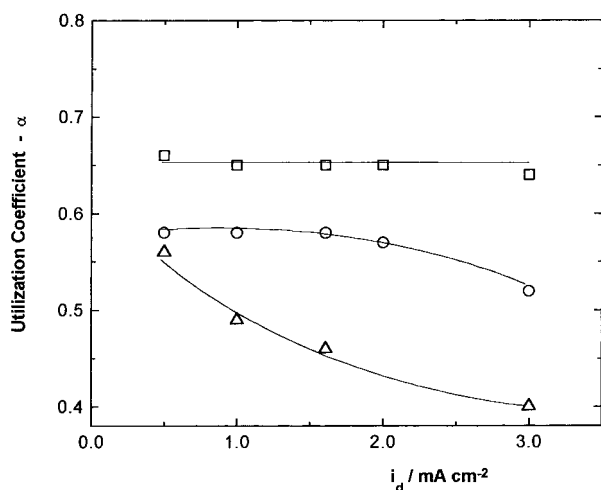


Fig. 10. Plots of the utilization coefficients for negative plates (A and H) against the discharge current density. Values for positive plates taken from [6] have also been plotted for comparison. In all cases the solution was 3.5 M  $\text{H}_2\text{SO}_4$ . Key: ( $\square$ ) negative plate A, ( $\circ$ ) negative plate H and ( $\triangle$ ) positive plate A.

oped about the variation on the nucleation with discharge conditions. This can be seen especially when the  $\alpha$  values for negative plates are compared with those obtained for positive plates [6]. These last ones have also been plotted in Figure 10, for comparison, under the same conditions. For positive plates,  $\alpha$  shows a continuous decrease, while for negative plates it remains practically constant except for the highest  $\text{H}_2\text{SO}_4$  concentration. The difference cannot be attributed to different concentration gradients inside the pores. The discharge rates were sufficiently slow and the macroporosity, for both positive and negative plates, were the same. If this is the accepted reason, there is no explanation for the constant region of  $\alpha$  in the negative plate.

Following the above discussion, the difference must be attributed to the mechanism of the solid state reaction that forms  $\text{PbSO}_4$  at the electrode/solution interface. The nucleation product on the positive plate would be  $\text{PbO}$  and there is no nucleation agent in this case. This implies that the number of nuclei will vary with the discharge conditions and, consequently, the thickness of the discharge product will change (see Figure 1 in [11]). For the negative plates, there is a nucleation agent and therefore the number of nuclei is practically constant, except at a high rate of discharge, as pointed out previously.

All these results have shown the importance of studying negative plates not only to understand them but also to compare them with the positive ones.

The variation of the energetic coefficient ( $\beta$ ) with sulfuric acid concentration, for A and H negative plates, is presented in Figure 11. This parameter was determined following the previous proposed methodology [6, 12]. Again, the equivalent results are given for positive plates from reference [6], for the purpose of comparison.  $\beta$  must be understood as the maximum amount of

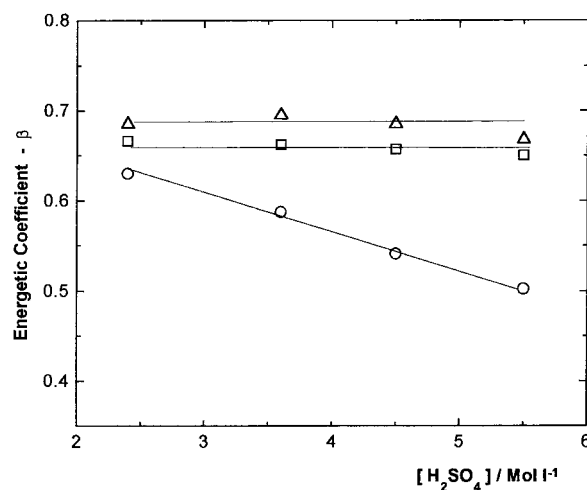


Fig. 11. Energetic coefficient against the acid concentration for the two different negative plates (A and H). Values for positive plates taken from [6] have also been plotted for comparison. Key: ( $\square$ ) negative plate A, ( $\circ$ ) negative plate H and ( $\triangle$ ) positive plate A.

charge that it is possible to obtain from a given active material divided by the theoretical amount.

As theoretically proposed and found in previous work for positive plates [6, 12],  $\beta$  values for the A negative plates are independent of sulfuric acid concentration. Nevertheless, the H negative plate shows unexpected behaviour. The  $\beta$  value in this case, in contrast to what happens with other positive and negative plates, decreases with increase in  $\text{H}_2\text{SO}_4$  concentration. This may be related to problems in the manufacturing technology. This is the first demonstration that  $\beta$  is not only a theoretically important parameter but also that it is related to manufacturing quality, as previously foreseen [6, 12].

The reasons for this decrease in the case of the H plate need further investigation, but a possible explanation can be advanced. Since  $\beta$  gives information about the 'active area of the plate' [6, 12], its decrease should be interpreted as a reduction in this active area. This could be related to the kind and size of the micropores. As the  $\text{H}_2\text{SO}_4$  concentration increases, part of the plate active surface may become inaccessible. This may happen, for example, if the entrances to some of the micropores became blocked. This possibility needs to be studied further.

#### 4. Conclusions

A general explanation for slow discharge of negative plates is proposed. In the plateau region of the discharge curve, as the overpotentials and the ohmic resistance were independent of the sulfuric acid concentration, a solid state reaction mechanism is proposed.

Through the idea of a solid state reaction as a film growth and the application of passivity theories, the small reduction in specific capacity of the negative plates with increasing sulfuric acid concentration is explained.

The logarithm of specific capacity versus discharge current density follows, as in positive plates, a linear relationship, permitting determination of the maximum possible amount of discharge. Through this it is shown that reactions in negative and positive plates must be different. The maximum possible amount of discharge in negative plates, against the situation in the positive ones, depends on the sulfuric acid concentration. This fact was explained, for the negative plates, in terms of the nucleation on  $\text{BaSO}_4$  particles and on the Pb. The higher decrease for positive plates is related to the nucleation of  $\text{PbO}$  on the  $\text{PbO}_2$  without a nucleation agent.

Furthermore, the decrease observed in the positive plate utilization coefficient with increase in discharge rate does not occur in the negative plates, except at the highest  $\text{H}_2\text{SO}_4$  concentration, in agreement with the previous explanation.

Finally, the results obtained for the energetic coefficient of negative plates from different manufacturers have shown that this parameter can denote some technical problems in the production process. Thus, as already theoretically proposed, the determination of the energetic coefficient could help to improve the manufacturing technology and the quality of lead acid batteries.

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